

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Treatment of Textile Materials and to New Compositions Comprising Cellulose Derivatives for Use therein.

We, JAMES CRAIK, of 4, Sandhills, Stevenston, Ayrshire, CECIL HERBERT LILLY, of Belmont, Mitchell Place, Saltcoats, Ayrshire, both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

The present invention relates to the treatment of textile materials, for example to finishing, combining and the like operations, and to new compositions comprising cellulose derivatives for use therein.

The inconvenience attendant on the use of viscose compositions has promoted the search for other cellulosic derivatives capable of being utilised in compositions for the treatment of textile materials, and numerous proposals have been made to employ finishing compositions based on alkaline solutions obtained from ethers or esters of cellulose of the kind characterised by their low content of the ether or ester group and by insolubility in water and in organic solvents. In such proposals the general method for the treatment has consisted in the application of the alkaline solution with or without filling or other effect materials to the textile material, and the subsequent regeneration of the cellulose derivative. Ethers and esters of cellulose are known which have a content of less than one ether or ester group for each $C_6H_{10}O_5$ molecule of cellulose, which are insoluble in water and organic solvents, which do not dissolve completely when simply mixed with sodium hydroxide solution, but which however are capable of being brought into solution in dilute sodium hydroxide by treating them therewith and subjecting the mixture to freezing and then allowing the temperature of the solution to rise, or by the use of a dispersing agent or another colloid soluble in alkaline solution, or by subjecting the mixture to the action of a colloid mill. In general the ethers and esters of cellulose thus cap-

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able of being brought into solution in sodium hydroxide solution are characterised by a still lower degree of substitution than those which are capable of being dissolved in normal fashion in dilute sodium hydroxide, and the cellulosic derivatives regenerated from them have a greater resistance to water. The cellulose esters and ethers so characterised yield finishes possessed of a superior degree of resistance to laundering conditions such as are liable to be encountered in normal usage of the finished textile material, and are therefore preferable. Amongst the cellulose esters and ethers which can be brought into solution in the above manner are glycol cellulose, methyl cellulose, cellulose glycollic acid and cellulose sulphates (see British Specifications Nos. 389,534; 410,152, 410,153; 416,590; 420,529 and 445,571).

Hitherto in making up compositions for treating textile materials the method has been to employ a sufficient concentration of aqueous sodium hydroxide to effect the practically complete disappearance of the fibres of cellulose derivatives, the syrupy solutions if necessary being filtered to remove any small amounts of undissolved fibre, whereupon the filling or other effect material may be incorporated. For the purpose of bringing about this solution the concentration of sodium hydroxide in water required is not independent of the desired concentration of the cellulose ether or ester, it being found that the greater the concentration of the cellulose ester or ether required, the greater is the minimum concentration of the sodium hydroxide required to effect its solution by whatever method is employed. The concentration of sodium hydroxide required however cannot be indefinitely reduced by reducing the proportion of the cellulose ester or ether to the dissolving medium. When an insufficient concentration of sodium hydroxide is present the fibrous cellulose derivative will remain wholly or partly undissolved.

The textile material treated with the compositions prepared from the syrupy

solutions of the cellulose ester or ether, after the regeneration of the cellulose derivative, exhibits a certain stiffness when dry corresponding to the concentration of the cellulose derivative in the composition applied, and when it is desired to produce a soft handle, treatment with a softening agent and/or treatment of the finished material by mechanical means has been required.

We have now found that when the syrupy solution obtained from the cellulose ether or ester of a low degree of substitution insoluble in water but capable of dissolving in or being brought into solution in dilute sodium hydroxide is subjected to a treatment sufficient to induce gelatinous properties in the syrup without causing complete gelation or deposition or separation of the cellulose derivative, textile finishing compositions may be obtained conferring a relatively soft handle upon the textile material to which they are applied. The compositions prepared from the solutions in which gelatinous properties have been induced further possess a higher covering power, which may be attributed to a smaller tendency to penetrate into the body of the textile threads or fibres, while the finishes obtained on the textiles retain a sufficient degree of resistance to mechanical action.

In putting our invention into effect, the necessary gelatinous properties may be induced by careful addition to the syrupy solution of the cellulose ether or ester of a quantity of water sufficient to reduce the sodium hydroxide concentration below that which would be required to effect solution of the cellulose ether or ester in the amount of liquor corresponding to the diluted solution, but insufficient to cause flocculation, separation or substantial lack of fluidity. Agitation during the addition is necessary. Thus for instance in the case of a glycol cellulose of the kind in which to prepare a 7% solution by the freezing method there is required a concentration of about 7.5% sodium hydroxide, and to prepare a 2 to 5% solution there is required about 4.5% to 5.5% sodium hydroxide, sufficient water may be introduced to bring the sodium hydroxide concentration somewhat below 4%. The appearance of the gelatinous properties may not be immediate, and in order to avoid the risk of adding too much water, which would ultimately lead to coagulation, it is advisable in determining the amount of water which should be added to examine the appearance after 1 to 3 hours of diluted test portions of the solution, by which time the gelatinous properties

will be manifest. Their appearance will be readily recognised by comparison with test portions diluted with corresponding amounts of sodium hydroxide of the concentration used in making up the original syrupy solutions.

Gelatinous properties may however also be induced by the addition of aqueous solutions of coagulating agents e.g. soluble salts, especially those of the alkali metals, water soluble organic liquids such as alcohol, or acetone. Aqueous solutions of even acid coagulants may be employed, for instance hydrochloric acid, ammonium salts, or acetic acid, but to avoid coagulation it may be necessary for these to be used in a highly dilute state. It is necessary in all cases to avoid high local concentrations of the coagulating agent added. The use of certain of the above materials reduces the amount of water which it is necessary to introduce into the solution, and may be preferable if it is desired to retain a comparatively high concentration of the cellulose derivative in the finishing composition.

Another method of inducing gelatinous properties is by heating the solution to a suitably elevated temperature. In this case the composition may be applied warm, but the composition may be heated to a higher temperature than that at which it is suitable for actual application, since even if sufficiently heated to gelate it too far, e.g. to a substantially rigid condition, it regains the necessary fluidity as it cools without entirely losing gelatinous properties.

Filling or other effect materials may be introduced either before or after the treatment inducing the appearance of the gelatinous properties. It is desirable that the treating composition should be allowed a short period of time to age before it is applied to the textile material. The application of the textile material may be carried out by spreading by means of a doctor, or otherwise in known manner, the cellulose derivative, being regenerated thereafter, for instance by treatment of the textile, if desired in the undried state, in a dilute aqueous acid bath. Once prepared and aged, the treating compositions of our invention are stable for long periods, when suitably stored, thus exhibiting a considerable advantage over compositions made from viscose.

Textile materials treated in accordance with our invention do not require the use of softening agents and/or mechanical treatment, and are characterised by a soft handle. When the compositions of the invention comprise

the cellulose esters and ethers of the kind which, while not dissolved by simple agitation with dilute sodium hydroxide are capable of being brought into solution therein by one or other of the methods described, the treated textiles retain a marked degree of permanency to laundering, and it is preferred to employ these materials for the purposes of the invention. It is further preferred to employ high viscosity samples.

The invention is further illustrated by the following examples:—

EXAMPLE 1.

Glycol cellulose is employed of the kind capable of forming a solution in dilute sodium hydroxide on subjecting a mixture of the glycol cellulose and the sodium hydroxide solution to freezing until crystals of ice appear, but not capable of completely dissolving in dilute sodium hydroxide solution on simple admixture at ordinary temperature. One part of such glycol cellulose is brought into solution in 20 times its weight of 5.3% sodium hydroxide solution by the method described. The solution is then slowly diluted with water until the concentration of glycol cellulose is 3%, the solution being agitated during the dilution. Two parts of china clay are then introduced. The solution is allowed to remain for an hour, after which the composition is spread on to a cotton

fabric by means of a doctor. The spread fabric is run through a bath of dilute sulphuric acid to regenerate the glycol cellulose, whereupon the fabric is washed and dried. The finished fabric is characterised by a soft handle.

EXAMPLE 2.

100 Parts of a solution of glycol cellulose obtained as described in Example 1 is brought into a gelatinous condition by the gradual introduction of 35—40 parts of a saturated solution of sodium chloride, which is gradually introduced with agitation. The gelatinous composition so obtained may be applied as a textile finish in the usual manner.

EXAMPLE 3.

7 Parts of methyl cellulose of the kind prepared by the method described in Example 2 of Specification No. 416,590 are dissolved in 93 parts of 10% sodium hydroxide solution, with the aid of a dispersing agent. The solution is then slowly diluted with 15% sodium chloride solution until the concentration of methyl cellulose is 4%. 10 Parts of talc are then added with stirring. After standing for 1—3 hours the mass is used for the treatment of cotton fabric on a spreading machine. A soft full handle is obtained.

Dated the 28th day of May, 1936.

E. C. G. CLARKE,
Solicitor for the Applicants.

COMPLETE SPECIFICATION.

Improvements in or relating to the Treatment of Textile Materials and to New Compositions Comprising Cellulose Derivatives for Use therein.

We, JAMES CRAIK, of 4, Sandhills, Stevenston, Ayrshire, and CECIL HERBERT LILLY, of Belmont, Mitchell Place, Saltcoats, Ayrshire, both British subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the treatment of textile materials, for example to finishing, multiplying and like operations.

The inconvenience attendant on the use of viscose compositions in these operations has promoted the search for other cellulose derivatives capable of being utilised in compositions for the treatment

of textile materials; and numerous proposals have been made to employ finishing compositions based on syrupy solutions in aqueous alkali of ethers or esters of cellulose of the kind characterised by a low content of the ether or ester group, by insolubility in water and in organic solvents, and by solubility in aqueous alkali. In such proposals the general method of treatment has consisted in the application of the alkaline solution, with or without filling or other effect materials, to the textile material, and the subsequent regeneration of the cellulose derivative on the fabric. Particular ethers and esters of cellulose are known which have the following characteristics; a content of less than one ether or ester group for each $C_6H_{10}O_5$ unit of cellulose; insolubility in water and organic solvents; incomplete solubility in sodium hydroxide solution

on simple mixing therewith; a capability of being brought into solution in dilute sodium hydroxide by treating them therewith and subjecting the mixture to freezing and then allowing the temperature of the solution to rise (see for example British Specification No. 389,534), or by subjecting the mixture to the action of a dispersing agent or another colloid soluble in alkaline solution or a colloid mill (British Specifications Nos. 410,152 and 410,153). In general, such ethers and esters of cellulose are characterised by a still lower degree of substitution than those which are capable of being dissolved in normal fashion in dilute sodium hydroxide, and the cellulosic derivatives regenerated from their solutions have a greater resistance to water. The cellulose esters and ethers so characterised yield finishes possessed of a superior degree of resistance to laundering conditions, such as are liable to be encountered in normal usage of the finished textile material, and are therefore preferable. Amongst the cellulose esters and ethers that can be obtained in forms requiring to be brought into solution in dilute aqueous alkali in the above manner are: glycol cellulose, methyl cellulose, cellulose glycollic acid and cellulose sulphates (see British Specifications Nos. 389,534; 410,152; 410,153; 416,590; 420,529 and 445,571).

Hitherto in making up compositions for treating textile materials the method has been to employ a sufficient concentration of aqueous sodium hydroxide to effect the practically complete dispersion of the fibres of cellulose derivatives, the syrupy solutions if necessary being filtered to remove any small amounts of undissolved fibre, whereupon the filling or other effect material may be incorporated. For the purpose of bringing about this solution the concentration of sodium hydroxide in water required is not independent of the desired concentration of the cellulose ether or ester, it being found that, the greater the concentration of the cellulose ester or ether solution required, the greater is the minimum concentration of the sodium hydroxide required to effect its solution by whatever method is employed. The concentration of sodium hydroxide required however cannot be indefinitely reduced by reducing the proportion of the cellulose ester or ether to the dissolving medium. When an insufficient concentration of sodium hydroxide is present, the fibrous cellulose derivative will remain wholly or partly undissolved or will gelate.

In the particular case of those cellulose esters or ethers of the kind which can be brought into complete solution by freez-

ing, it is generally known that the employment of an insufficient concentration of sodium hydroxide leads to gelation of the solution when the temperature is allowed to rise.

The textile material treated with the compositions prepared from the syrupy solutions as described above, exhibits, after regeneration of the cellulose derivative, a certain stiffness when dry corresponding to the concentration of the cellulose derivative in the composition applied; when it is desired to produce a soft handle, treatment with a softening agent and/or treatment of the finished material by mechanical means has been required.

We have now found that when the syrupy solution, obtained from the cellulose ether or ester of a low degree of substitution insoluble in water but capable of dissolving in or being brought into solution in dilute sodium hydroxide, is subjected to a treatment sufficient to induce gelatinous properties in the syrup without causing complete gelation or deposition or separation of the cellulose derivative, textile finishing compositions may be obtained conferring a relatively soft handle upon the textile material to which they are applied. The compositions prepared from the solutions in which gelatinous properties have been induced further possess a higher covering power, which may be attributed to their smaller tendency to penetrate into the body of the textile threads or fibres, and the finishes obtained on the textiles retain a sufficient degree of resistance to damage by mechanical action.

In the treatment of textile material with a viscous composition it has been proposed to employ the composition in a state of increased viscosity and incipient coagulation brought about by the addition of a coagulating agent. Owing, however, to the natural progressive and irreversible hydrolysis, and consequent viscosity increase, of cellulose xanthate solutions, the effect produced by a given quantity of a coagulating agent is dependent upon the history of the solution treated, and in particular on its original composition, age and conditions of storage, and in endeavouring to effect a routine coagulation to a predetermined and critical degree it is difficult to ensure reproducible results. We have found, however, that in spite of any viscosity changes due to storage, solutions in alkali of cellulose ethers or esters having solubility characteristics of the kind described can be employed satisfactorily and with reproducible results in a state of incipient coagulation brought about

by the routine addition of a given quantity of coagulating agent, which quantity need not be modified to take account of the history of the particular sample of solution undergoing treatment.

5 The present invention consists in a process for the treatment of fabrics or like textile materials by applying a cellulose derivative composition to the textile material and regenerating the cellulose derivative thereon, the cellulose derivative composition comprising a cellulose ester or ether of a low degree of substitution and insoluble in water which has been brought into the form of a syrupy solution in dilute aqueous caustic alkali and subsequently treated in such a manner as to induce gelatinous properties therein without, however, causing complete gelation or any deposition of the cellulose derivative. The term "gelatinous properties" as employed herein and in the appended claims denotes that the viscosity of the solution of the cellulose derivative in aqueous alkali is increased substantially over and above that of an untreated solution, the viscosity comparison being made between solutions having the same concentration of the cellulose derivative.

10 In producing the cellulose derivative composition, the necessary gelatinous properties may be induced by careful addition to the syrupy solution of the cellulose ether or ester of a quantity of water sufficient to reduce the sodium hydroxide concentration below that which would be required to effect solution of the cellulose ether or ester in the amount of liquor corresponding to the diluted solution, the quantity of water added being however insufficient to cause flocculation, separation or substantial lack of fluidity. Agitation during the addition is necessary. Thus for instance into a solution of a glycol cellulose of the kind in which to prepare a 7% solution by the freezing method there is required a concentration of about 7.5% sodium hydroxide, and to prepare a 2% to 5% solution there is required about 4.5% to 5.5% sodium hydroxide, sufficient water may be introduced to bring the sodium hydroxide concentration somewhat below 4%. The appearance of the gelatinous properties may not be immediate, and in order to avoid the risk of adding too much water, which would ultimately lead to coagulation, it is advisable in determining the amount of water which should be added to examine the appearance of diluted test portions of the solution after 1 to 3 hours, by which time the gelatinous properties will be manifest. Their appearance will be readily recognised by comparison with

test portions diluted with corresponding amounts of sodium hydroxide of the concentration used in making up the original syrupy solutions.

70 Gelatinous properties may however also be induced by the addition of aqueous solutions of coagulating agents e.g. soluble salts (especially those of the alkali metals), or water soluble organic liquids such as alcohol or acetone. Aqueous solutions of even acid coagulants may be employed, for instance hydrochloric acid, ammonium salts, or acetic acid, which will form salts in presence of alkali; to avoid local coagulation it may be necessary for these acid coagulants to be used in a highly dilute state. It is necessary in all cases to avoid high local concentrations of the coagulating agent added. The use of certain of the above materials reduces the amount of water which it is necessary to introduce into the solution, and may be preferable if it is desired to retain a comparatively high concentration of the cellulose derivative in the finishing composition.

90 Another method of inducing gelatinous properties is by heating the solution to a suitably elevated temperature. In this case the composition may be applied warm, but the composition may be heated to a higher temperature than that at which it is suitable for actual application, since even if sufficiently heated to gelate it too far, e.g. to a substantially rigid condition, it regains the necessary fluidity as it cools without entirely losing gelatinous properties.

95 Filling or other effect materials may be introduced either before or after the treatment inducing the appearance of the gelatinous properties. It is desirable that the treating composition should be allowed a short period of time to age before it is applied to the textile material.

100 The application of the textile material may be carried out by spreading by means of a doctor, or otherwise in known manner, the cellulose derivative being regenerated thereafter, for instance by treatment of the textile, if desired in the undried state, in a dilute aqueous acid bath. Once prepared and aged, the treating compositions of our invention are stable for long periods, when suitably stored, thus exhibiting a considerable advantage over compositions made from viscose.

105 Textile materials treated in accordance with our invention do not require the use of softening agents and/or mechanical treatment, and are characterised by a soft handle. When the compositions of the invention comprise the cellulose esters

and others of the kind which, while not dissolved by simple agitation with dilute sodium hydroxide are capable of being brought into solution therein by one or other of the methods described, the treated textiles retain a marked degree of permanency to laundering, and it is preferred to employ these materials for the purposes of the invention. It is further preferred to employ high viscosity samples.

The invention is further illustrated by the following Examples.

EXAMPLE 1.

Glycol cellulose is employed of the kind capable of forming a solution in dilute sodium hydroxide on subjecting a mixture of the glycol cellulose and the sodium hydroxide solution to freezing until crystals of ice appear, but not capable of completely dissolving in dilute sodium hydroxide solution on simple admixture at ordinary temperatures. One part of such glycol cellulose is brought into solution in 20 times its weight of 5.3% sodium hydroxide solution by the method described. The solution is then slowly diluted with water until the concentration of glycol cellulose is 3%, the solution being agitated during the dilution. Two parts of china clay are then introduced. The solution is allowed to remain for an hour, after which the composition is spread on to a cotton fabric by means of a doctor. The spread fabric is run through a bath of dilute sulphuric acid to regenerate the glycol cellulose, whereupon the fabric is washed and dried. The finished fabric is characterised by a soft handle.

EXAMPLE 2.

100 parts of a solution of glycol cellulose obtained as described in Example 1 is brought into a gelatinous condition by the gradual introduction of 35-40 parts of a saturated solution of sodium chloride, which is gradually introduced with agitation. The gelatinous composition so obtained may be applied as a textile finish and regenerated in the usual manner.

EXAMPLE 3.

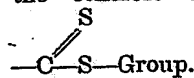
7 parts of methyl cellulose of the kind prepared by the method described in Example 2 of Specification No. 416,590 are dissolved in 93 parts of 10% sodium hydroxide solution, with the aid of a dispersing agent. The solution is then slowly diluted with 15% sodium chloride solution until the concentration of methyl cellulose is 4%. 10 parts of talc are then added with stirring. After standing for 1-3 hours the mass is used for the treatment of cotton fabric on a spreading

machine. After regeneration, a soft, full handle is obtained.

EXAMPLE 4.

A 5% glycol cellulose solution in 5.3% sodium hydroxide made as described in Example 1 is mixed with one tenth of its weight of a gold simulating metal powder of the bronze powder type, and the solution is heated while agitating to a temperature of 50 C., and is applied to the surface of a cotton cloth in a spreading machine at a temperature of 45-50° C. The sprayed fabric is run through a bath of sulphuric acid from which it is rapidly removed and washed in water and dried.

The term "cellulose ester or ether" as used herein is not intended to include the cellulose derivatives containing the



Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:-

1. A process for the treatment of fabrics or like textile materials by applying a cellulose derivative composition to the textile material and regenerating the cellulose derivative thereon, the cellulose derivative composition comprising a cellulose ester or ether of a low degree of substitution and insoluble in water which has been brought into the form of a syrupy solution in dilute aqueous caustic alkali and subsequently treated in such a manner as to induce gelatinous properties therein without, however, causing complete gelation or any deposition of the cellulose derivative.

2. A process as claimed in claim 1 in which the cellulose ester or ether is incapable of complete solution in dilute aqueous alkali by simple admixture therewith at ordinary temperature, the said cellulose ester or ether having been brought into solution by freezing and subsequent thawing, or by the use of a dispersing agent, or by subjecting the mixture to the action of a colloid mill.

3. A process as claimed in claim 1 or 2 in which for the purpose of inducing the desired gelatinous properties the solution of cellulose ester or ether is diluted with water with simultaneous agitation.

4. A process as claimed in claim 1 or 2 in which for the purpose of inducing the desired gelatinous properties the solution of cellulose ester or ether is treated with a water soluble coagulant with simultaneous agitation.

5. A process as claimed in claim 1 or 2 in which for the purpose of inducing the

desired gelatinous properties in viscosity the solution of cellulose ester or ether is subjected to a raised temperature.

5 6. A process for the treatment of fabrics or other textile materials substantially as hereinbefore described with reference to the examples.

10 7. A process for the production of cellulose derivative compositions suitable for use in the processes claimed in any of the preceding claims, which consists in bringing the cellulose ester or ether into the form of a syrupy solution in dilute aqueous caustic alkali and thereafter
15 treating the solution in such manner as to induce gelatinous properties therein without however causing complete gelation or any deposition of the cellulose derivative.

20 8. A process as claimed in claim 7

according to which the increase in viscosity is effected by adding to the solution with agitation a water soluble coagulant e.g. an alkali metal salt.

9. A process for the production of cellulose derivative compositions suitable for the treatment of fabrics or other textile materials substantially as hereinbefore described with reference to the examples. 25

10. Cellulose derivative compositions 30 whenever prepared by the processes claimed in any of claims 7, 8 or 9.

11. Fabrics or other textile materials 35 whenever treated by the processes claimed in any of claims 1 to 6 or with the compositions claimed in claim 10.

Dated the 28th day of May, 1937.

E. C. G. CLARKE,
Solicitor for the Applicants.

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